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(54) Title: REGENERATION OF ACETYLENE CONVERTER CATALYSTS BY HYDROGEN STRIPPING

(57) Abstract

An improved method for regenerating acetylene hydrogenation catalysts, particularly palladium based catalysts which have been used to remove acetylenic contaminants from ethylene, which method does not require an oxygenation or other pre-treatment step, comprises stripping the spent catalyst with hydrogen at 315-400 °C and a linear hydrogen-containing gas velocity of at least 15.2 cm/second, to achieve substantially complete regeneration.

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REGENERATION OF ACETYLENE CONVERTER
CATALYSTS BY HYDROGEN STRIPPING

BACKGROUND OF THE INVENTION

5

Field of the Invention

The present invention relates to an improved
method for regenerating catalysts that have been used
10   to remove acetylenic contaminants from olefin product
streams. More particularly, the present invention
relates to an improved method for regenerating
palladium-containing catalysts that have been used to
remove acetylenic contaminants from ethylene.

15

Product streams of liquid or liquefiable olefins
and diolefins typically are contaminated with small
amounts of acetylenic impurities. For example, the
ethylene/ethane fraction in an ethylene plant
20   typically contains 0.5 - 2.0% acetylenic impurities.
Such acetylenic contamination is undesirable because
acetylene tends to poison the catalysts that are used
to convert ethylene to polyethylene. Acetylene also
can form metal acetylides which are explosive and
25   which may contaminate the equipment that is used to
process such product streams.

It is known that acetylenic impurities can be
selectively hydrogenated and thereby removed from such
30   a product streams by passing the product stream over a
catalyst (an "acetylene hydrogenation catalyst") in
the presence of hydrogen; however, the hydrogenation
process typically results in the deposition of a green
oil on the catalyst which deactivates the catalyst.

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Therefore, acetylene hydrogenation processes typically
include an oxygenation step or a "burn" step to remove
the deactivating carbonaceous residues from the
catalyst followed by a hydrogen reduction step to

5   reactivate the catalyst. See, e.g., US-A-3,812,057
(Morgan) and US-A-4,424,255 (Toyoda).

An oxygenation step followed by hydrogen
reduction normally is effective to regenerate an

10   acetylene hydrogenation catalyst; however, there are
many disadvantages to the use of an oxygenation step
during regeneration of such catalysts.

First, when oxygen and hydrogen come together

15   under the conditions used to regenerate the catalyst,
an exothermic reaction is produced which may result in
uncontrolled temperature runaway. Thus, before the
regeneration is performed, it is necessary to purge
the catalyst of hydrogen and hydrocarbons using an

20   inert gas, such as nitrogen gas, both before and after
the oxygen-containing stream is introduced. The
purging process is both tedious and time consuming.
Furthermore, if the regeneration is performed in situ,
the concentration of oxygen in the regeneration gas

25   stream must be regulated carefully in order to avoid
reactor temperature run-away. It would be
advantageous if acetylene hydrogenation catalysts
could be regenerated using a method which did not
require such time consuming purging and monitoring.

30
The use of an oxygenation step during
regeneration of an acetylene hydrogenation catalyst
also presents an environmental concern due to the
resulting emission of carbon monoxide, carbon dioxide,

and unburned hydrocarbons. The hydrocarbon residue
that remains on the catalyst can comprise up to 10 wt%
of the catalyst. The oxygenation of this amount of
residue results in the emission of a substantial

5   amount of carbon monoxide and carbon dioxide. In
addition, the emission during oxygenation may contain
approximately 6-10% of unburned hydrocarbons. It
would be advantageous if acetylene reduction catalysts
could be regenerated in a manner that did not result

10   in such environmentally undesirable emissions.

       Regeneration of acetylene hydrogenation catalysts
using an oxygenation step also is undesirable because
the oxygenation step has a negative impact on the life

15   of the catalyst. A catalyst that has been used to
hydrogenate acetylene typically must be regenerated
once every one to three months. Acetylene
hydrogenation catalysts are heat sensitive, and
exposure to excessive heat decreases the activity of

20   the catalyst. The oxygenation step that is used in
most regeneration processes typically is run at
temperatures between 371-455°C (700-850°F). The
exposure of an acetylene hydrogenation catalyst to
such high temperatures at such regular intervals takes

25   a great toll on the life of the catalyst. It would be
advantageous if the regeneration of such catalysts
could take place at lower temperatures which reduced
the thermal stress induced during the regeneration.

30   Some of these disadvantages can be avoided if the
catalyst is regenerated ex situ, or outside of the
reactor. However, the unloading and reloading of the
reactor with the catalyst is a time consuming process.
Even if the regeneration process is performed ex situ,

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the catalyst still must be purged with an inert gas
both before unloading and after reloading the reactor.
Thus, regardless of where the regeneration process
takes place, significant reactor down time is required
5   if the catalyst is regenerated using a process that
includes an oxidation step.

For all of these reasons, it would be
advantageous if acetylene reducing catalysts could be
10   regenerated without an oxygenation step. Col. 4,
lines 16-35 of US-A-3,912,789 acknowledges that
partial regeneration can be accomplished using a
hydrogenation step alone. However, this patent
teaches that full regeneration of an exhausted
15   catalyst requires an oxygenation step. Therefore, a
process has yet to be developed that can fully
regenerate acetylene reduction catalysts without the
need for an oxygenation step.

20   Not only is an oxygenation step undesirable, but
any additional step in the regeneration procedure is
undesirable because each step requires a change of
conditions and switch over techniques which can be
deleterious to the performance or longevity of the
25   regenerated catalyst. For example, GB-1,158,418
teaches a method of regenerating hydrogenation
catalysts comprising a hydrocarbon wash step followed
by a hydrogen treatment. Indeed this patent discusses
an already known method consisting of contacting
30   hydrogen with the catalyst at an elevated temperature
(p. 1, line 77 - p. 2, line 10), but reports that this
known method was still insufficient to restore
completely the initial activity of the selective
hydrogenation catalyst.

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US-A-2,946,829 discloses a process of making a
Pd/Al$_2$O$_3$ catalyst for selective hydrogenation, used
with the industry standard method of regeneration,
5   which uses steam to provide heat to attain the needed
temperature to burn the polymeric deposits off the
catalyst. When a small amount of air is mixed into
the steam (see Example 3, col. 5, l. 52-55), the
resulting catalyst is relatively free of carbonaceous
10   deposits. The main function of the hydrogen reduction
step is to reduce the oxidized metal back to its
metallic state. In fact, the hydrogen reduction step
is not even required, as shown in Example 3, col. 5,
l. 65. On day 17, regeneration 6 did not include a
15   reduction step. The catalyst nevertheless was put
back on stream after steam treatment and exhibited
very high activity, i.e., at a space velocity of 2,000
and 150°F, acetylene in the reactor outlet dropped
from an inlet concentration of 0.35% to 1.3 ppm. This
20   compares favorably to the results of the first
regeneration, Example 1, which did use a hydrogen
reduction step after steam treatment -- 5 ppm
acetylene at the reactor outlet at a much lower space
velocity of 1,000 and 130°F.
25

In addition, US-A-2,946,829 teaches the need for
vigorous regeneration in order to remove polymer
deposits. Such severe regeneration leads to a loss of
physical strength in the hydrogenation catalyst, or to
30   impaired activity or selectivity (col. 2, lines 30-
37). The vigorous step in the disclosure is the step
of burning off the polymer deposits in the presence of
steam -- not the hydrogen reduction step. Thus, this

art teaches that the steam treatment step is essential
to regeneration of a hydrogenation catalyst.

5   GB-A-907,348 teaches the partial regeneration of
a nickel catalyst using a hydrogen treatment.
Although a temperature range of 200-600°C is
mentioned, all of the actual regenerations described
are carried out at temperatures in the range of 204-
250°C. In the Provisional Specification of GB-A-
10   907,348, temperatures at the lower end of the range
are said to be preferred, particularly 200-300°C.
From the actual experiments of GB-A-907,348,
regeneration at 250°C did not cause recovery of fresh
catalyst activity, and the stability of the
15   regenerated catalyst was lower except in the
experiment that used the lowest temperature (204°C).
(See Examples 1-3.) The failure to recover the
activity of fresh catalyst is clear because a higher
temperature is required to maintain the same hydrogen
20   consumption during regeneration (Example 1, 127°C
fresh v. 143°C regenerated; Example 2, 127°C fresh v.
138°C regenerated). And, in Examples 1 and 2 (which
used a regeneration temperature of 250°C), the
stability of the regenerated catalyst is lower
25   (Example 1, fresh catalyst required 152°C after 670
hours v. regenerated catalyst required 166°C after 477
hours; Example 2, fresh catalyst required 127°C after
335 hours v. regenerated catalyst required 138°C after
127 hours). However, in Example 3 (which regenerates
30   the catalyst at a temperature of 204°C), although the
activity of the fresh catalyst is not completely
recovered, the stability of the regenerated catalyst
is higher than the stability of the fresh catalyst
(regenerated catalyst required 142°C after 1410 hours,

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fresh catalyst required 160°C after 327 hours). Thus
this publication teaches away from the regeneration of
catalysts using hydrogen at temperatures that are
above 250°C.

5   SUMMARY OF THE INVENTION
        According to the present invention there is
provided a method of substantially completely
regenerating a catalyst that has been used to remove
acetylenic impurities from an olefin stream and which
10   has become at least partially deactivated by that use,
which comprises substantially stripping the
deactivated catalyst of carbonaceous deposits using
hydrogen at a linear velocity of at least 15.2
cm/second (0.5 feet per second), at a temperature of
15   from 315 - 400°C (599 - 750°F) and at other conditions
such that substantially complete regeneration is
effected, wherein said stripping is essentially the
only regeneration treatment employed and occurs in the
absence of an oxygenation step.
20

        It is a feature of the invention that acetylene
reduction catalysts can be substantially fully
regenerated by hydrogen stripping, alone, at
relatively low temperatures which are nevertheless
25   greater than those taught away from in prior art such
as GB-A-907,348. It has also been found that
palladium-containing catalysts that have been used to
purify ethylene unexpectedly have a better selectivity
to ethylene after they are hydrogen stripped according
30   to the present invention.

            BRIEF DESCRIPTION OF THE DRAWINGS
        Fig. 1 is a chart showing the Temperature
Programmed Oxidation (TPO) spectra of the UCI G58B

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catalyst of Example 1 before (a) and after (b)
hydrogen stripping.

Fig. 2 is a bar graph comparing the catalyst
activity of the BASF H011 catalyst of Example 2 before
and after hydrogen stripping. "SOR" under the first
bar in the graph stands for activity at the start of
the run. "EOR" under the second bar in the graph
stands for activity at the end of the run. The bar
above "662°F H2" represents the activity of the
substantially completely regenerated catalyst after
hydrogen stripping according to the invention at about
350°C (662°F). The bar above "788°F H2" represents the
(reduced) activity of the incompletely regenerated
catalyst after further hydrogen stripping outside the
scope of the invention at about 420°C (788°F).

Fig. 3(a) is a graph comparing the acetylene
conversion activity of the UCI G58E catalyst of
Example 3 when fresh to the activity of that same
(substantially completely regenerated) catalyst after
it has been hydrogen stripped according to the present
invention at about 350°C (662°F).

Fig. 3(b) is a graph comparing the deactivation
rate of the fresh and stripped catalyst of Example 3.

Fig. 3(c) is a graph comparing the selectivity to
ethylene of the fresh and stripped catalyst of Example
3.

Fig. 3(d) is a graph comparing the selectivity to
ethane of the fresh and stripped catalyst of Example
3.

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Fig. 3(e) is a graph comparing the selectivity to hydrocarbons having four or more carbon atoms of the fresh and stripped catalyst of Example 3.

DETAILED DESCRIPTION OF THE INVENTION

Preferably the at least partially deactivated (spent) acetylene hydrogenation catalyst is hydrogen stripped with a mixture of hydrogen and inert gas. When pure hydrogen is not used, the hydrogen concentration in such mixtures may be from 0.1 to less than 100%, preferably from 5 to 10%. Since a stripping gas having only 5-10% of hydrogen may be used during the stripping process, any low value hydrogen source, preferably without carbon monoxide, can be employed. For example, hydrogen may be purchased and mixed fresh with an inert gas, or the hydrogen may come from another refining operation. For example, the overhead effluent from a demethanizer, which contains about 5% H_2 in CH_4 (normally used as fuel gas) may be one potential source for hydrogen. It also may be possible to recycle hydrogen that has already been used to regenerate the catalyst.

The percentage of hydrogen in the gas stripping mixture is not critical to the present invention. In the following examples, a mixture of inert gas and around 9-10% hydrogen was used. Any inert gas may be used in the mixture. The most commonly available and most inexpensive inert gas for use in the invention is nitrogen; therefore, nitrogen is a preferred inert gas for use in the present invention.

Although the following examples of the invention
describe regeneration of palladium based acetylene
reduction catalysts, one of skill in the art will
recognize that the hydrogen stripping process of the
5   present invention may be used to regenerate other
types of catalysts that are used to hydrogenate acety-
lene. For example the present process could be used
to regenerate acetylene hydrogenation catalysts which
contain: Group VIII metals, such as nickel, cobalt,
10   ruthenium, palladium, and platinum; Group VIB metals,
such as chromium, molybdenum, and tungsten; or Group
IB metals, such as copper, silver, or gold. However,
the preferred catalyst for use in the present
invention is a catalyst in which the primary active
15   element is palladium, preferably one where palladium
comprises approximately 0.01-0.5% by weight of the
catalyst, more preferably 0.02-0.05%. A palladium
content higher than about 0.5% could deteriorate at
the temperatures used in the process of the present
20   invention. Optionally the palladium may be combined
with another metal, such as silver.

The catalyst metal is typically carried on a
support such as silica or alumina.
25
The stripping procedure of the invention takes
place at a temperature of from 315-400°C (600-750°F),
preferably between about 315-372°C (600-700°F), and
more preferably at about 350°C (662°F). In order to
30   avoid deactivating the catalyst, especially a
palladium based catalyst, or agglomerating the
palladium, the temperature of the hydrogen stripping
procedure should not exceed about 400°C. The
temperature should be at least 315°C to achieve the

substantially complete regeneration which is
commercially desirable, and other process conditions
will be readily determinable to enable this objective
to be reached.

5

The pressure at which the stripping takes place
may not be critical; however, the stripping preferably
takes place between atmospheric pressure (0 psig) and
2.07 MPag (300 psig), and more preferably between
10   atmospheric pressure and 345 kPag (50 psig). Lower
cost hydrogen sources having a low content of hydrogen
typically are more readily available at lower
pressures. In the following examples, pressures of
about 2.07 MPag and atmospheric pressure were used.
15   Similarly, the time period required for stripping is
not critical, save it should be sufficient to achieve
substantially complete regeneration. One of skill in
the art will recognize that the amount of time needed
for the stripping procedure can be determined by
20   monitoring the amount of hydrocarbon present in the
catalyst until a minimum plateau level has been
achieved. In the following examples, the stripping
time ranged between 16-24 hrs.

25   The flow rate of the hydrogen through the
catalyst should be such that the linear velocity
through the catalyst should be at least about 15.2
cm/second (0.5 feet/second). This will ensure
uniformity of reactant concentrations and temperatures
30   throughout the reactor during regeneration. It has
been found that lower velocities may be insufficient
to achieve uniform regeneration of the catalyst. The
parameter of linear velocity is used herein rather
than, e.g., space velocity because linear velocity

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commonly is used to calculate dispersion and mixing
phenomena in packed beds. For example, the axial and
radial dispersion of reactant concentration are
estimated by calculating Peclet numbers (James
5   Carberry, "Chemical and Catalytic Reaction
Engineering", p. 162). The linear velocity also is an
important factor in controlling heat transfer in the
reactor. Furthermore, linear velocities may differ
even where the space velocity remains the same. For
10   example, wide and shallow beds will have lower linear
velocities than narrow and deep beds will have.
However, narrow and deep beds will have a higher
pressure drop than wide and shallow beds. Thus, it is
desirable to specify either linear velocity or space
15   velocity with the reactor L/D ratio to ensure proper
design or scale up of the reactor.

It is a feature of the invention that
substantially complete regeneration is achieved
20   without the need for an additional or associated
regeneration step, e.g., hydrocarbon wash or steam
treat or, particularly, oxygenation. As shown in
Example 1 which follows, the process of the invention
enables catalyst to be re-used as fresh catalyst after
25   regular hydrogen only regenerations of the catalytic
metal sites, preferably in situ in the acetylene
reduction reactor. Nevertheless it may be desirable
from time to time to clean carbonaceous deposits from
the support (as opposed to the catalyst metal) because
30   hydrogen stripping does not remove all of the
carbonaceous deposits from the support. Thus it is
possible that an air burn may be desirable eventually
in order to clean the support to prevent restriction
of flow rate, pressure, etc. However, the number of

air burns that may be employed to clean the supports
in such a system will be much less than the frequent
air burns that heretofore have been required to
regenerate the catalyst. An infrequent air burn to
5   clean the support will be much less intrusive and
damaging than the frequent, repetitive air burns
required in current catalyst regeneration processes.

The following examples illustrates the invention.
10

EXAMPLE 1

An aliquot of UCI G58B catalyst (Pd/Al$_2$O$_3$),
deactivated after 200 hours of use as an acetylene
hydrogenation catalyst in olefin stream treatment, was
15   stripped with 10% H$_2$/Ar at linear velocity greater
than 15.2 cm/sec and at a temperature which rose from
room temperature to about 750°C (1382°F) at a heating
rate of about 13 degrees C/min (23.4°F/min). The
carbonaceous residues on the catalyst were analyzed
20   both before and after hydrogen stripping by
temperature programmed oxidation (TPO), which detected
carbon oxide emission during the TPO burn while the
reactor temperature was linearly increased. The TPO
spectra of the spent catalyst before and after
25   hydrogen stripping were plotted as Figure 1(a) and
(b), respectively.

Before hydrogen stripping, two types of
carbonaceous residues were present on the catalyst. A
30   peak at about 400°C (750°F) represents carbonaceous
residues that were present on and/or near palladium.
A peak at about 510°C (950°F) represents carbonaceous
residues that were present on the support. After
hydrogen stripping, only one peak appeared at 550°C

(1022°F). The presence of only this single peak after
hydrogen stripping indicated that the carbonaceous
residues that were on and/or near the palladium were
removed by the hydrogen stripping. Since acetylene

5   conversion occurs mainly on palladium sites in the
catalyst, the removal of carbonaceous residues from
the palladium can re-expose the palladium active sites
and recover substantially all the activity of the
palladium. The hydrocarbons that are stripped off the

10   catalyst can be either recycled to the cracker or used
as fuel gas.

                          EXAMPLE 2
       A BASF HO11 catalyst (Pd/SiO$_2$) was subjected for

15   200 hours to the reaction conditions of 1.5% wt C$_2$H$_2$
(in an olefinic stream), 1.6 H$_2$/C$_2$H$_2$ molar ratio, 4000
gas hourly space velocity (GHSV), 2.07 MPag (300
psig), and about 66°C (151°F) average bed temperature.
After 200 hours, the acetylene conversion of the

20   catalyst decreased from 79% to 58%. The spent
catalyst was then regenerated by hydrogen stripping
for 16 hours with 5% H$_2$/N$_2$ at 2.07 MPag (300 psig) and
greater than 15.2 cm/sec linear velocity in the
reactor, and about 350°C (662°F). After the hydrogen

25   stripping, the acetylene conversion of the catalyst
was 78%. A comparison of the catalyst activity before
and after hydrogen stripping is plotted in Figure 2.
The results indicate that the hydrogen stripping at
about 350°C (662°F) substantially fully regenerated

30   the catalyst.

       The temperature used during hydrogen stripping is
preferably not too high or else the palladium will
begin to agglomerate and will not achieve

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substantially complete regeneration using only a
hydrogen treat step. For example, when the catalyst
was further hydrogen stripped at about 420°C (788°F)
for 16 hours, under otherwise the same conditions, the
5   activity of the catalyst was reduced to 62% acetylene
conversion -- a dramatic decrease in catalyst
activity.

EXAMPLE 3
10   A spent UCI G58E catalyst (Pd/Ag/Al$_2$O$_3$) which had
been used for acetylene hydrogenation in an ethylene
stream was hydrogen stripped at about 350°C (662°F)
and 1 atmosphere pressure with 9% H$_2$/N$_2$ at linear
velocity in the reactor of greater than 15.2 cm/sec,
15   for 24 hours. The performance of the hydrogen
stripped catalyst was then compared to the performance
of fresh catalyst at 70 hours into the activity test.
The results are tabulated in Table I. The parameters
of the activity test carried out in a normal
20   hydrogenation reactor were 1.4% wt C$_2$H$_2$, 1.2 H$_2$/C$_2$H$_2$
molar ratio, 4900 GHSV, 2.07 MPag (300 psig), about
102°C (215°F) sand-bath temperature.

TABLE I

	Fresh	H$_2$ Stripped
C$_2$H$_2$ Conversion	80%	80%
Selectivity to C$_2$H$_4$	57%	67%
Selectivity to C$_2$H$_6$	32%	23%
Selectivity to C$_4$+	11%	10%
Deactivation Rate	-0.1%/hr	-0.2%/hr

As seen from Table I, the spent catalyst which had been hydrogen stripped according to the invention unexpectedly had a selectivity to ethylene that was 10 points better than the selectivity of the fresh

5   catalyst. Also, the ethane make was substantially reduced after hydrogen stripping. This result suggests that a "de-edging" process may have occurred which reduced the number of palladium sites responsible for over hydrogenating acetylene/ethylene

10   to ethane.

Although the deactivation rate was higher for the hydrogen stripped catalyst, the deactivation rate can be overcome by more frequent hydrogen stripping. Even

15   if more frequent hydrogen stripping is required to regenerate catalyst, the present process may be less time consuming and less damaging to the catalyst than frequent air burns or other additional treatment steps.

20

CLAIMS:

1.   A method of substantially completely
regenerating a catalyst that has been used to remove
acetylenic impurities from an olefin stream and which
has become at least partially deactivated by that use,
which comprises substantially stripping the
deactivated catalyst of carbonaceous deposits using
hydrogen at a linear velocity of at least 15.2
cm/second (0.5 feet per second), at a temperature of
from 315 - 400°C (599 - 750°F) and at other conditions
such that substantially complete regeneration is
effected, wherein said stripping is essentially the
only regeneration treatment employed and occurs in the
absence of an oxygenation step.

2.   The method of claim 1 wherein the
temperature is from 315 - 372°C (600 - 700°F),
preferably about 350°C (662°F).

3.   The method of claim 1 or 2 wherein the
hydrogen stripping employs a gas comprising an inert
gas, preferably nitrogen, and from 5 to 10% of
hydrogen.

4.   The method of any preceding claim wherein
the catalyst comprises palladium, optionally together
with another metal.

5.   The method of claim 4 wherein the palladium
comprises from 0.01 to 0.5 wt%, preferably from 0.02
to 0.05% of the catalyst.

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6.   The method of any preceding claim wherein
the catalyst has been used to remove acetylenic
impurities from ethylene.

5   7.   The method of claim 6 wherein after
regeneration the catalyst is used to remove acetylenic
impurities from ethylene and the selectivity of the
catalyst to ethylene is enhanced.

10   8.   The method of any preceding claim wherein
the catalyst comprises a silica or alumina support.
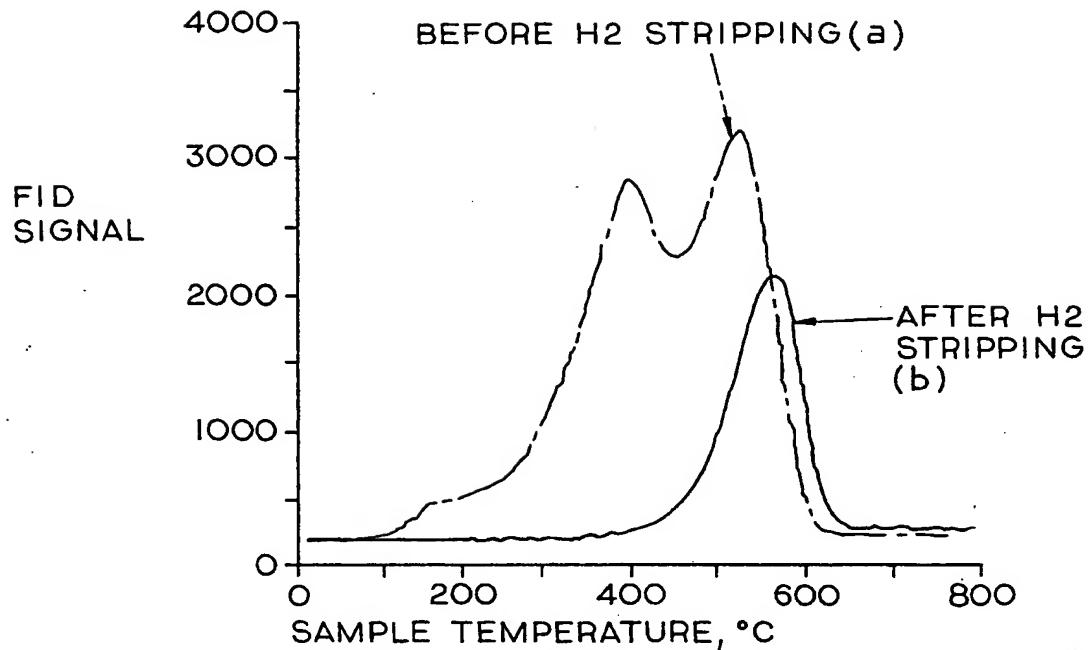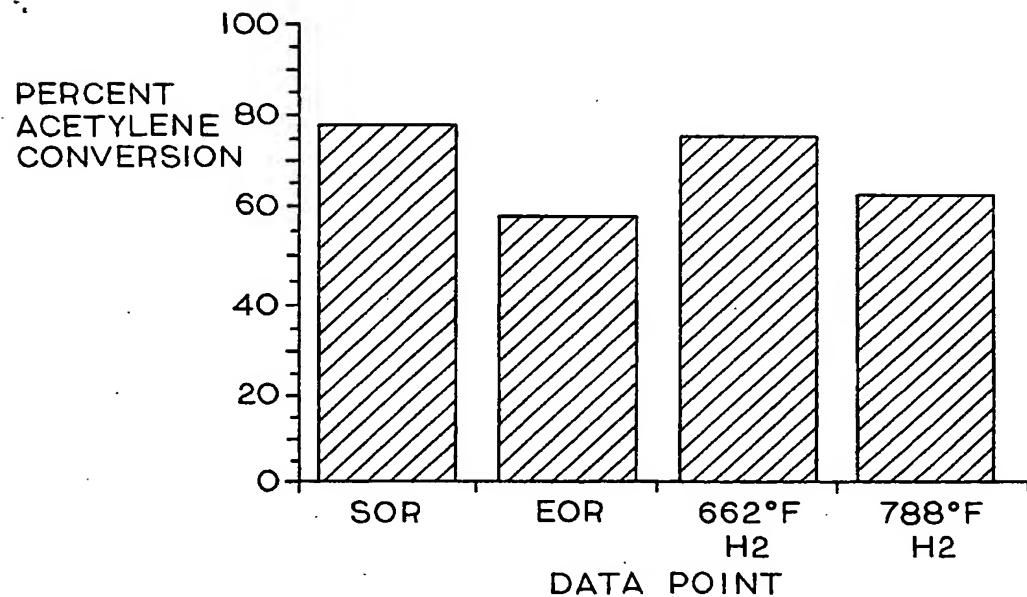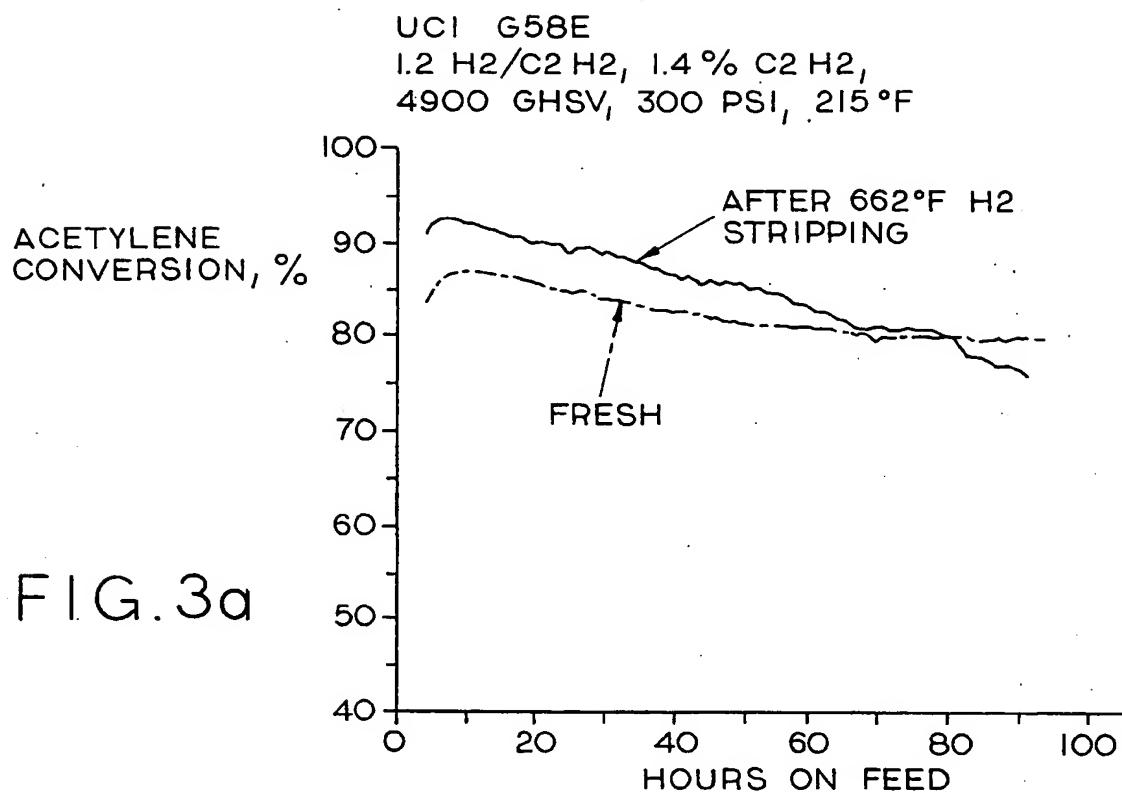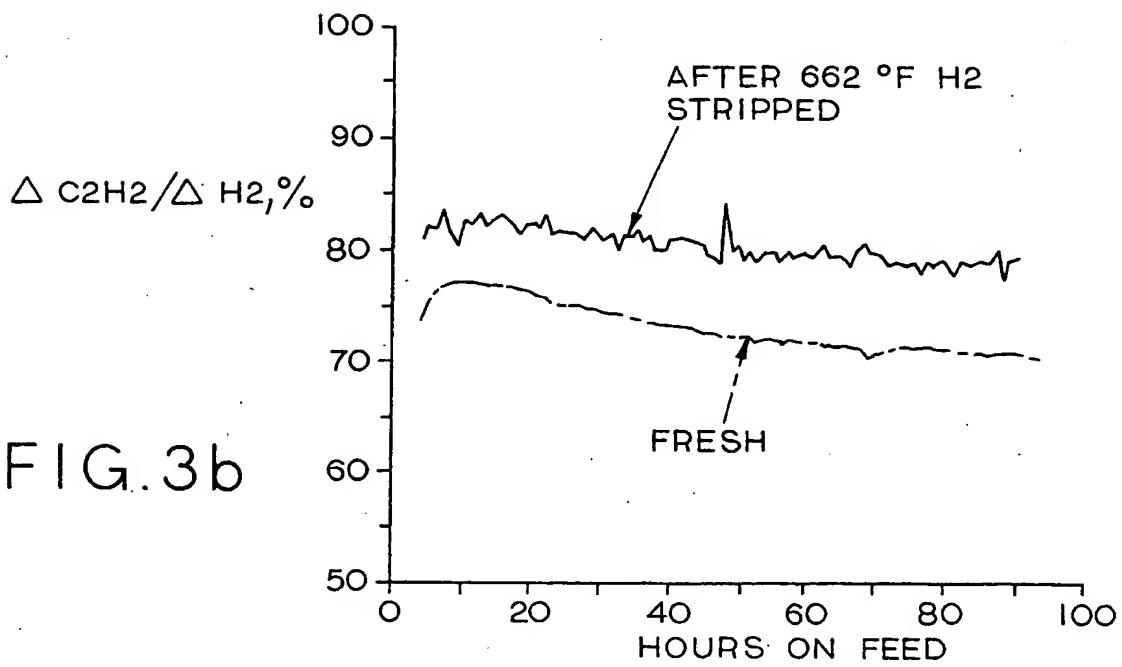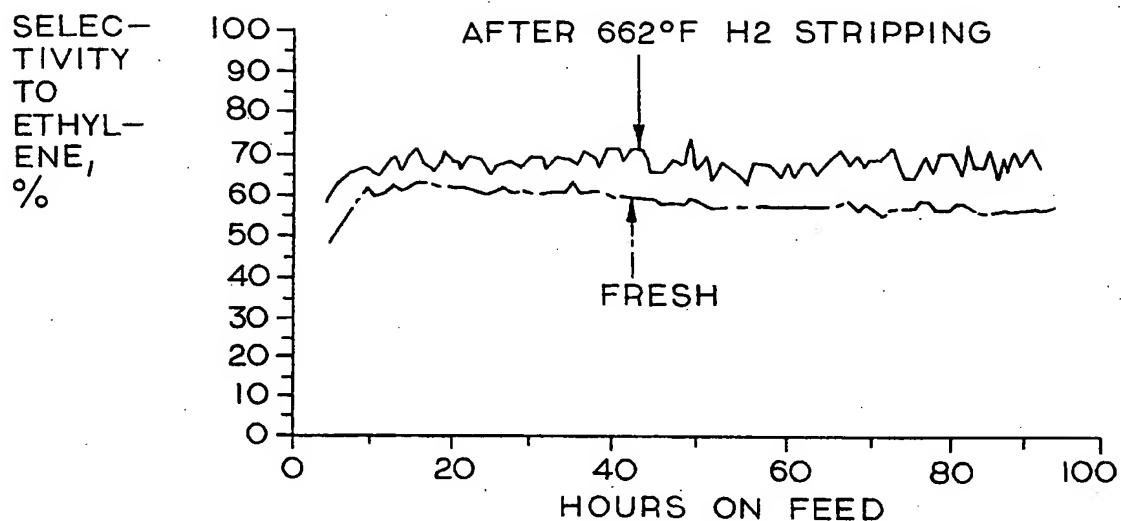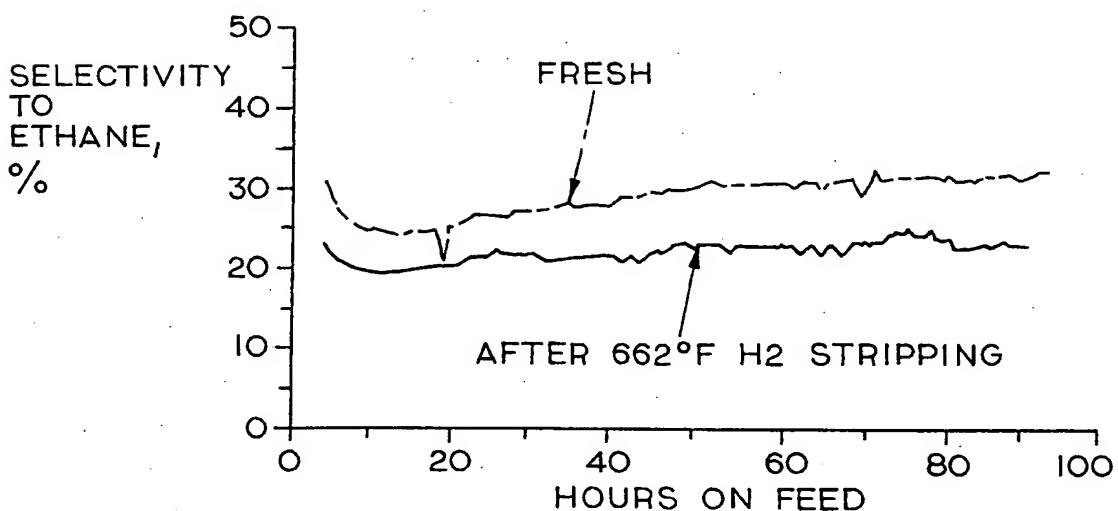
FIG.1


FIG.2

-2/4-

UCI G58E
1.2 H2/C2 H2, 1.4 % C2 H2,
4900 GHSV, 300 PSI, 215°F

ACETYLENE
CONVERSION, %

AFTER 662°F H2
STRIPPING

FRESH

FIG.3a

HOURS ON FEED

△ C2H2/△ H2,%

AFTER 662 °F H2
STRIPPED

FRESH

FIG.3b

HOURS ON FEED

SUBSTITUTE SHEET

SELEC-
TIVITY
TO
ETHYL-
ENE,
%

AFTER 662°F H2 STRIPPING

FRESH

HOURS ON FEED

FIG.3c

SELECTIVITY
TO
ETHANE,
%

FRESH

AFTER 662°F H2 STRIPPING

HOURS ON FEED

FIG.3d
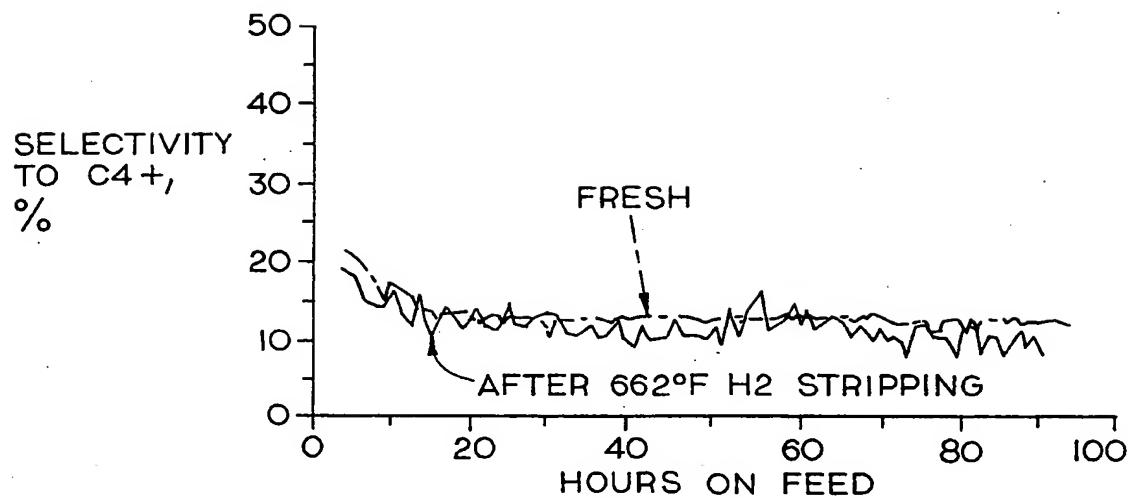
FIG. 3e

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: B01J 23/96, B01J 38/10, C07C 7/167
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: B01J, C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 1048343 (ESSO RESEARCH AND ENGINEERING COMPANY), 16 November 1966 (16.11.66), page 1, line 20 - line 29; page 3, line 45 - line 48, claims 1,5	1,3-5,8
A	DE, A1, 4022852 (BASF AG), 23 January 1992 (23.01.92), claims 1,3	1-8
A	DE, A1, 3022043 (BASF AG), 24 December 1981 (24.12.81), claim 1	1-8

☒ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
30 Sept 1993	29. 10. 93

Name and mailing address of the International Searching Authority	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Bengt Christensson

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 3893942 (CHANG-LEE YANG), 8 July 1975 (08.07.75), column 5, line 53 - line 55, claim 1	1-8

INTERNATIONAL SEARCH REPORT
Information on patent family members

26/08/93

5390

International application No.

PCT/US 93/05880

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB-A-	1048343	16/11/66	DE-B-	1276009	00/00/00
			NL-A-	295598	00/00/00
			US-A-	3238120	00/00/00
DE-A1-	4022852	23/01/92	EP-A-	0467176	22/01/92
			JP-A-	4227063	17/08/92
			US-A-	5143872	01/09/92
DE-A1-	3022043	24/12/81	EP-A,B-	0042097	23/12/81
			JP-A-	57024642	09/02/82
			US-A-	4379756	12/04/83
US-A-	3893942	08/07/75	BE-A-	820398	26/03/75
			CA-A-	1029048	04/04/78
			DE-A-	2445881	24/04/75
			FR-A,B-	2245587	25/04/75
			GB-A-	1482694	10/08/77
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